

Superconducting properties of Pr-based filled skutterudite $\text{PrRu}_4\text{As}_{12}$

Takahiro NAMIKI^{1*}, Yuji AOKI², Hideyuki SATO², Chihiro SEKINE¹, Ichimin SHIROTANI¹, Tatsuma D. MATSUDA³,
Yoshinori HAGA³, Takehiko YAGI⁴

¹ Faculty of Engineering Science, Muroran Institute of Technology, 27-1 Mizumoto, Muroran, Hokkaido 050-8585, Japan

² Department of Physics, Graduate School of Science, Tokyo Metropolitan University, Minami-Ohsawa 1-1, Hachioji, Tokyo 192-0397, Japan

³ Advanced Science Research Center, Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan

⁴ Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba 277-8581, Japan

We report on a systematic study of the superconducting characteristics and Pr crystalline-electric-field (CEF) levels of the filled skutterudite $\text{PrRu}_4\text{As}_{12}$ ($T_c = 2.33$ K). The temperature dependences of the upper critical field H_{c2} and the Ginzburg-Landau (Maki) parameter κ_2 suggest *s*-wave clean-limit superconductivity. The electronic specific heat coefficient $\gamma \sim 95$ mJ/K²mol, which is ~ 1.5 times larger than that of $\text{LaRu}_4\text{As}_{12}$, indicates *4f*-originating quasiparticle mass enhancement. The magnetic susceptibility $\chi(T)$ indicates that the CEF ground state is a Γ_1 singlet and a $\Gamma_4^{(1)}$ triplet first excited state lies at $\Delta_{\text{CEF}} \sim 30$ K above. A systematic comparison among $\text{PrOs}_4\text{Sb}_{12}$, $\text{PrRu}_4\text{Sb}_{12}$, $\text{PrRu}_4\text{As}_{12}$, and La-based reference compounds suggests that the inelastic exchange scattering and aspherical charge scattering of conduction electrons from CEF-split *4f* levels play an essential role in the quasiparticle mass enhancement and in determining the value of T_c in the Pr-based filled skutterudites.

KEYWORDS: Filled skutterudite, $\text{PrRu}_4\text{As}_{12}$, specific heat, susceptibility, superconductivity, crystal electric field

Among heavy-fermion superconductors, the filled skutterudite $\text{PrOs}_4\text{Sb}_{12}$ has attracted considerable attention for its unconventional superconducting (SC) properties.^{1,2} Some of the characteristic features are broken time-reversal symmetry,³ odd parity,⁴ possible structure in the SC gap,^{5,6} multi band superconductivity,⁷ and adjacent quadrupole ordering and its fluctuations (quadrupole excitons).^{8–11} In contrast, $\text{PrRu}_4\text{Sb}_{12}$ is a conventional BCS-type superconductor as suggested by a coherence peak in the NQR spin-lattice relaxation rate $1/T_1$.¹² Systematic understanding for such variety in the SC properties of Pr-based filled skutterudites is one of the important issues (see Table II for a summary of the SC parameters).

It has been pointed out that the crystalline electric field (CEF) level scheme of Pr ions may play an essential role. In the T_h site symmetry, the $J = 4$ multiplet of Pr^{3+} ions splits into four sublevels,¹³ namely, a singlet Γ_1 , a non-Kramers nonmagnetic doublet Γ_{23} , and two triplets $\Gamma_4^{(1)}$ and $\Gamma_4^{(2)}$. $\text{PrOs}_4\text{Sb}_{12}$ has Γ_1 ground state with a $\Gamma_4^{(2)}$ first excited state with the energy separation $\Delta_{\text{CEF}} = 8$ K.^{11,14} In contrast, $\text{PrRu}_4\text{Sb}_{12}$ has $\Gamma_1 - \Gamma_4^{(1)}$ levels with $\Delta_{\text{CEF}} = 65$ K.^{15–17} The differences in the type of the first excited state and Δ_{CEF} may be a key reason for the different SC properties.

In this paper, we report the specific heat and magnetic susceptibility measurements of another Pr-based filled skutterudite $\text{PrRu}_4\text{As}_{12}$ ¹⁸ to study the SC properties and the CEF level scheme. The results indicate that the superconductivity is of the conventional BCS type with a moderate quasiparticle mass enhancement. A systematic comparison among these Pr-based compounds and their

Table I. Fractional coordinates and Debye-Waller factors U_{eq} of $\text{PrRu}_4\text{As}_{12}$ determined from the single-crystal x-ray diffraction data.

atom	site	x	y	z	$U_{\text{eq}}(\text{\AA}^2)$
Pr	2a	0	0	0	1.082(4)
Ru	8c	1/4	1/4	1/4	0.294(3)
As	24g	0	0.14954(3)	0.35019(3)	0.387(5)

La-based references reveals that inelastic scatterings of conduction electrons from CEF-split *4f* levels play an essential role for the SC properties and quasiparticle mass enhancement in the Pr-based filled skutterudites.

Polycrystalline $\text{PrRu}_4\text{As}_{12}$ samples are synthesized using stoichiometric amounts of 3N(99.9% pure)-Pr, 4N-Ru, and 5N-As powders by the high-pressure and high-temperature method (~ 4 GPa at 900 °C).¹⁹ Powder x-ray diffraction indicates the inclusion of a small amount of the RuAs_2 phase; the maximum peak height of RuAs_2 is approximately 10 % of that of $\text{PrRu}_4\text{As}_{12}$. The structural parameters of $\text{PrRu}_4\text{As}_{12}$ are determined by single-crystal x-ray diffraction using an imaging plate detector with Mo K_α radiation. A small single crystal with approximate dimensions of $0.10 \times 0.07 \times 0.05$ mm is selected from the ingot. The structural parameters are successfully refined based on the 179 independent reflections with the agreement factor $\sum ||F_o| - |F_c|| / \sum |F_o| = 0.023$, where F_o and F_c are the experimental and calculated structure factors, respectively. Fractional coordinates and Debye-Waller factors (U_{eq}) are listed in Table I. The obtained lattice constant of 8.491(4) Å agrees with a reported value.²⁰ $U_{\text{eq}}(\text{Pr})$ is ~ 3 times larger than $U_{\text{eq}}(\text{Ru})$ and $U_{\text{eq}}(\text{As})$. Note that $U_{\text{eq}}(\text{Pr})$ in $\text{PrRu}_4\text{As}_{12}$ is larger than that in $\text{PrRu}_4\text{P}_{12}$,²¹ indicating larger ther-

*E-mail address: namiki@mmm.muroran-it.ac.jp

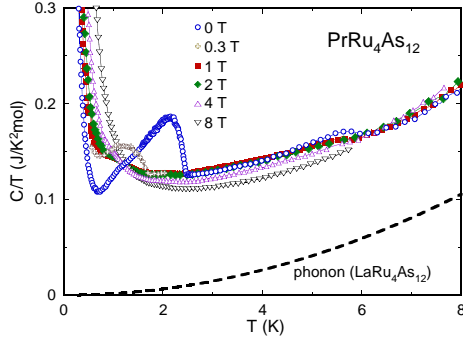


Fig. 1. (Color online) Specific heat divided by temperature (C/T) of $\text{PrRu}_4\text{As}_{12}$ measured in several magnetic fields. The broken curve represents the phonon part C_{ph}/T determined for $\text{LaRu}_4\text{As}_{12}$.¹⁸

mal vibrations of Pr ions in As_{12} cages, whose size is larger than that of P_{12} cages.

The specific heat $C(H, T)$ is measured by a quasiadiabatic heat pulse method⁸ using a dilution refrigerator equipped with an 8 T SC magnet. The temperature increment caused by each heat pulse is controlled to $\sim 2\%$ for the usual measurement and to $\sim 0.5\%$ in limited temperature ranges where the SC transition occurs. The magnetic susceptibility χ is measured in $1.8 < T < 300$ K using an SC quantum interference device (SQUID) magnetometer (Quantum Design Inc.).

The temperature dependence of C/T measured in selected magnetic fields is shown in Fig. 1. In zero field, a clear jump appears at the SC transition temperature $T_c = 2.33$ K, which is very close to a resistively determined value of 2.4 K.¹⁸ With increasing field, T_c shifts to lower temperatures and the size of the jump becomes smaller (for details, see the inset of Fig. 2).

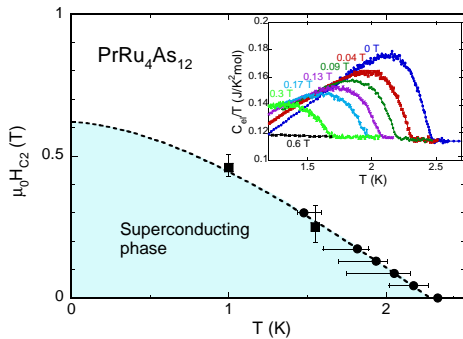


Fig. 2. (Color online) Upper critical field $\mu_0 H_{c2}$ vs T determined by T -sweep and H -sweep measurements of C . The error bars denote the 10% – 90% width of the specific heat jump. The broken line shows the best-fit WHH curve (see text). The inset shows C_{el}/T vs T near T_c .

In the measured temperature range, C consists of three terms, namely, the electronic contribution (C_{el}), phonon contribution (C_{ph}), and nuclear Schottky contribution (C_{n}). In zero field, $C_{\text{n}} = A(H)/T^2$ appears as a low- T upturn below 0.7 K. This term gradually develops with increasing field. The phonon term $C_{\text{ph}} = \beta T^3$ with

$\beta = 1.53 \text{ mJ/K}^4\text{mol}$ determined for $\text{LaRu}_4\text{As}_{12}$ ¹⁸ is indicated by the broken curve in Fig. 1. By the fitting using $C(T, H) = C_{\text{el}}(T, H) + A(H)/T^2 + \beta T^3$, $C_{\text{el}}(T, H)$ is extracted (see the inset of Fig. 2).

Note that there appears a slight jump at $T_A \sim 6$ K in zero field. This anomaly is probably due to a magnetic ordering in a secondary phase included in the present sample since no corresponding anomalies appear in recent ^{75}As -NQR measurements.²² This phase has not been identified by the x-ray diffraction measurements. To synthesize a sample free from the secondary phase, sample preparation is conducted several times under different conditions and the best sample is used for the present measurements. Probably due to the contamination of the secondary phase, C/T decreases with increasing field in the normal state, making it difficult to estimate the electronic specific heat coefficient (γ). Nevertheless, from the C data at 8 T, where the contribution of the secondary phase is largely suppressed, $\gamma \sim 95 \text{ mJ/K}^2\text{mol}$ is estimated. The specific heat jump $\Delta C/\gamma T_c \sim 0.83$, smaller than 1.43 for a weak-coupling BCS superconductor, and apparent $\sim T^2$ dependence in $C(T)$ below T_c may suggest SC gap anisotropy or multi band superconductivity. However, a clear coherence peak observed in As-NQR $1/T_1$ indicates that such nonuniformity would not be very large.²²

From the $C_{\text{el}}(T, H)$ data, the upper critical field $\mu_0 H_{c2}(T)$ is determined, as shown in the H -vs- T phase diagram of Fig. 2. It appears that the $\mu_0 H_{c2}(T)$ curve is well reproduced by the Werthamer-Helfand-Hohenberg (WHH) formula for the clean limit^{23,24} with the initial slope $[-d(\mu_0 H_{c2})/dT]_{T_c} = 0.365 \text{ T/K}$. This fact indicates that $\mu_0 H_{c2}$ is mainly determined by the orbital effect and the spin Pauli paramagnetic effect does not play a dominant role; the Pauli limiting field is $\mu_0 H_P = 3.9 \text{ T} \ll \mu_0 H_{c2}$. The $T = 0$ value of $\mu_0 H_{c2}$ is estimated to be $\sim 0.62 \text{ T}$ by the WHH fitting.

There appears a slight upward deviation in the $\mu_0 H_{c2}(T)$ curve below 0.05 T, leading to an enhancement in T_c by 2% in zero field compared with the best-fit WHH curve for $\mu_0 H > 0.05 \text{ T}$. A similar behavior is observed in the case of $\text{PrOs}_4\text{Sb}_{12}$ ²⁸ and $\text{YNi}_2\text{B}_2\text{C}$,²⁹ indicating that the upward deviation in T_c may come from the multi band effect.

By combining the $\mu_0 H_{c2}$ and $\Delta C/T_c$ data, the Ginzburg-Landau parameter (or Maki parameter)³⁰ κ_2 is determined using the thermodynamical relation:

$$\Delta C/T_c = \left[\frac{d(\mu_0 H_{c2})}{dT_c} \right] \times \frac{1}{4\pi(2\kappa_2^2 - 1)\beta_A}, \quad (1)$$

where β_A is 1.16 for a triangular vortex lattice.³¹ The result is shown in Fig. 3. The value of κ_2 is ~ 10 at $T = T_c$ (in zero field) and increases with decreasing temperature.³² The behavior of $d\kappa_2/dT < 0$ is again consistent with the negligible Pauli paramagnetic depairing effect mentioned above; for superconductors with a strong Pauli paramagnetic effect, $d\kappa_2/dT > 0$ appears (e.g., CeCoIn_5 ; see Ref. 33). The temperature dependence of κ_2 is affected by impurity scatterings.³⁴ In the clean limit, the theoretical parameter $\kappa_2(T)$ diverges as $T \rightarrow 0$ with $\kappa_2 \propto \sqrt{\ln(T_c/T)}$ ^{30,35} as shown in Fig. 3.

Table II. Superconducting parameters of Pr-based filled skutterudites and their isostructural La-based reference compounds.

Material	T_c (K)	$\mu_0 H_{c2}$ (T)	$[-\frac{dH_{c2}}{dT}]_{T_c}$ (T/K)	Δ_{CEF} (K)	First excited state	γ (mJ/K ² mol)	m_c^*/m_0 for γ -branch	Reference
PrRu ₄ As ₁₂	2.33	0.62	0.37	~ 30	$\Gamma_4^{(1)}$	95		This work
LaRu ₄ As ₁₂	10.3	0.72	0.08			73		18
PrRu ₄ Sb ₁₂	1.03	0.2	0.24	65	$\Gamma_4^{(1)}$	59	1.6	15, 16, 25
LaRu ₄ Sb ₁₂	3.58	0.28	0.12			37	1.4	15, 16
PrOs ₄ Sb ₁₂	1.81	2.3	1.9	8	$\Gamma_4^{(2)}$	~ 500	7.6	1, 11, 26
LaOs ₄ Sb ₁₂	0.74	0.04	0.095			55	2.8	26, 27

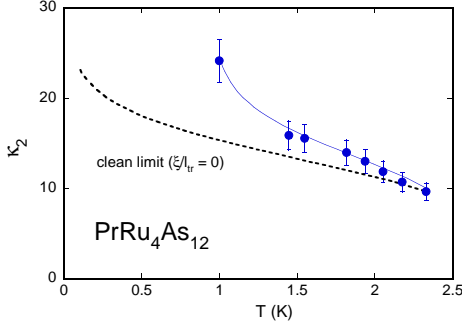


Fig. 3. Temperature dependence of Ginzburg-Landau parameter (Maki parameter) κ_2 for PrRu₄As₁₂. The broken curve indicates the theoretical curve for the clean limit. The solid curve is a guide to the eye.

However, in the dirty limit, the temperature dependence of κ_2 is largely suppressed ($\kappa_2(0)/\kappa_2(T_c) \sim 1.2$). The $\kappa_2(T)$ data in Fig. 3 indicates that the present sample is rather close to the clean limit.

The magnetic susceptibility $\chi(T)$ is shown in Fig. 4. At high temperatures, $\chi(T)$ can be well described by

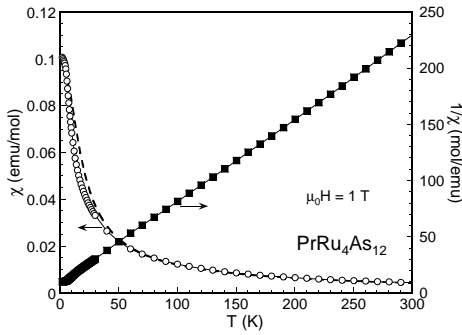


Fig. 4. Temperature dependences of susceptibility χ (open circle) and inverse susceptibility χ^{-1} (open square). The dashed line shows the best-fit CEF model calculation (see text).

a Curie-Weiss law $\chi = N_A \mu_{eff}^2 / 3k_B(T - \Theta_{CW})$, where the effective magnetic moment $\mu_{eff} = 3.30\mu_B/\text{f.u.}$ and the Curie-Weiss temperature $\Theta_{CW} = -11$ K. The obtained μ_{eff} value is close to the Pr³⁺ free-ion value ($3.58\mu_B/\text{Pr}$), indicating a well-localized character of Pr 4f electrons. Below ~ 10 K, $\chi(T)$ shows a deviation from the Curie-Weiss law, exhibiting a saturation tendency. This behavior suggests that the low-lying CEF level scheme of Pr³⁺ ions has a Γ_1 singlet ground state and a $\Gamma_4^{(1)}$ triplet

first excited state. Note that in the case of a $\Gamma_4^{(2)}$ first excited state, as realized in PrOs₄Sb₁₂, a maximum should appear in $\chi(T)$.^{1,8} This interpretation agrees with the electronic entropy $S_{el}(T, H)$ (not shown) calculated from the $C_{el}(T, H)$ data. S_{el} at 8 K is less than 20 % of $R \ln 2$, ruling out the possibility of any degenerate ground states. In the measured temperature range, dS_{el}/dH is always negative. In PrOs₄Sb₁₂, $dS_{el}/dH > 0$ is observed below 3 K.⁸ This behavior is caused by the Zeeman splitting of the low-lying triplet first excited state at $\Delta_{\text{CEF}} = 8$ K. This fact indicates that $\Delta_{\text{CEF}} \gg 8$ K for PrRu₄As₁₂. For a rough estimation of the low-lying CEF level scheme, a least-squares fit has been made based on the O_h Lea-Leask-Wolf scheme³⁶ (omitting the $O_6^2 - O_6^6$ term characteristic of the T_h site symmetry in the CEF Hamiltonian). The best overall fit of the $\chi(T)$ data (shown by the dashed line in Fig. 4) corresponds to a Γ_1 ground state with a Γ_4 ($\Gamma_4^{(1)}$ in T_h) triplet excited state at $\Delta_{\text{CEF}} \sim 30$ K.³⁷ For an accurate determination of the overall CEF level scheme, inelastic neutron scattering measurements would be necessary.

Only for LaOs₄Sb₁₂, among the three systems shown in table II, an enhancement in T_c is caused by the replacement of La by Pr ions. This behavior may be accounted for by considering the predominant type of conduction-electron scatterings from Pr 4f electrons. Fulde *et al.*³⁸ have theoretically demonstrated that inelastic aspherical charge scattering (ACS) associated with 4f quadrupole moments leads to an increase in T_c , while exchange scattering (ES) decreases T_c . For a qualitative discussion, a comparison with the theoretical calculation is made in Fig. 5. For LaOs₄Sb₁₂, since the first excited state of the replaced Pr ions is $\Gamma_4^{(2)}$ ($\sim \Gamma_5$ in O_h having large off-diagonal quadrupole moments with Γ_1), the ACS may dominate over the ES. Furthermore, $\Delta_{\text{CEF}}/2T_c(\text{LaOs}_4\text{Sb}_{12}) \simeq 5$ happens to be the best condition for the enhancement in T_c . On the other hand, in LaRu₄As₁₂ and LaRu₄Sb₁₂, the first excited state of the replaced Pr ions is $\Gamma_4^{(1)}$ ($\sim \Gamma_4$ in O_h having large off-diagonal dipole moments with Γ_1) and the resulting predominant ES will cause a strong pair-breaking effect, thereby decreasing T_c .

The quasiparticle mass enhancement is also expected to be caused by the interactions of conduction electrons with low-lying CEF levels. Flude *et al.* have proposed a model for the mass enhancement due to virtual CEF excitations:³⁹

$$\frac{m^*}{m_0} - 1 = (g_J - 1)^2 J_{sf}^2 N(0) \frac{2|\langle i|J|j \rangle|^2}{\Delta_{\text{CEF}}}, \quad (2)$$

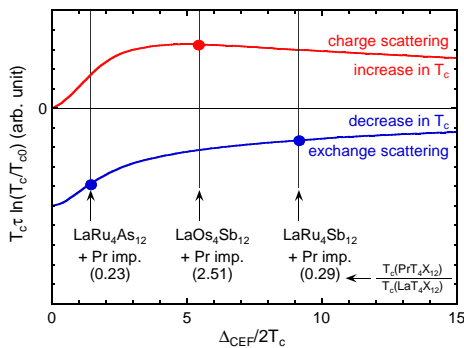


Fig. 5. (Color online) Two curves showing calculated changes in T_c vs $\Delta_{\text{CEF}}/2T_c$ by doping impurity ions with singlet-singlet CEF levels (see Ref. 38 for the parameter definition). For a rough estimation of the Pr doping effect on T_c , $\Delta_{\text{CEF}}/2T_c$ for $\text{LaT}_4\text{X}_{12}$ is indicated. The expected dominant scattering process is indicated by solid circles.

where g_J is the Landé factor, J_{sf} is the exchange integral coupling the conduction electrons to the f electrons, $N(0)$ is the bare conduction electron density of states at the Fermi level, and $\langle i|J|j\rangle$ is the magnetic dipole matrix element calculated using the derived CEF parameters. Figure 6 shows several physical quantities that provide measures of the mass enhancement as a function of Δ_{CEF} . There appears a rough trend of $m^*/m - 1 \propto$

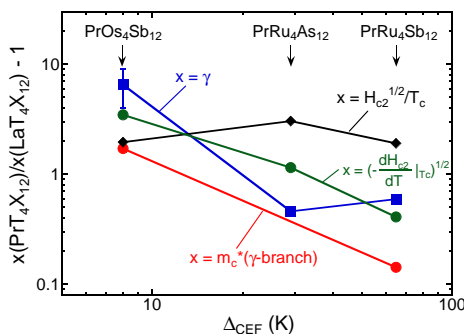


Fig. 6. (Color online) Mass enhancement factor $m^*/m_0 - 1$, estimated from several physical quantities, is plotted as a function of Δ_{CEF} .

$1/\Delta_{\text{CEF}}$ in Fig. 6. However, as discussed above for the effect on T_c , not only the ES process but also the ACS process should contribute to the mass enhancement with a different prefactor of $1/\Delta_{\text{CEF}}$. In $\text{PrOs}_4\text{Sb}_{12}$, the importance of quadrupolar degrees of freedom is inferred from a strong correlation between quadrupolar excitons and superconductivity.¹¹ Further experimental and theoretical studies on the role of quadrupoles in Pr-based filled skutterudites will be needed.

We thank M. Ichioka, Y. Kohori, H. Kusunose, N. K. Sato, K. Takeda, and Y. Yanase for fruitful discussions. This work was partially supported by a Grant-in-Aid for Scientific Research Priority Area “Skutterudite” (Nos. 15072101, 15072206, 18027002) of MEXT, Japan Scientific Research (c) (No. 17540309) of MEXT, Japan.

- 1) E. D. Bauer, N. A. Frederick, P.-C. Ho, V. S. Zapf, and M. B. Maple: Phys. Rev. B **65** (2002) 100506.
- 2) For a review, see, for example, Y. Aoki, T. Tayama, T. Sakakibara, K. Kuwahara, K. Iwasa, M. Kohgi, W. Higemoto, D. E. MacLaughlin, H. Sugawara, and H. Sato: J. Phys. Soc. Jpn. **76** (2007) 051006.
- 3) Y. Aoki, A. Tsuchiya, T. Kanayama, S. R. Saha, H. Sugawara, H. Sato, W. Higemoto, A. Koda, K. Ohishi, K. Nishiyama, and R. Kadon: Phys. Rev. Lett. **91** (2003) 067003.
- 4) W. Higemoto, S. R. Saha, A. Koda, K. Ohishi, R. Kadono, Y. Aoki, H. Sugawara, and H. Sato: Phys. Rev. B **75** (2007) 020510(R).
- 5) K. Izawa, Y. Nakajima, J. Goryo, Y. Matsuda, S. Osaki, H. Sugawara, H. Sato, P. Thalmeier, and K. Maki: Phys. Rev. Lett. **90** (2003) 117001.
- 6) J. Custers, Y. Namai, T. Tayama, T. Sakakibara, H. Sugawara, Y. Aoki, and H. Sato: Physica B **378–380** (2006) 179.
- 7) G. Seyfarth, J. P. Brison, M.-A. Méasson, J. Flouquet, K. Izawa, Y. Matsuda, H. Sugawara, and H. Sato: Phys. Rev. Lett. **95** (2005) 107004.
- 8) Y. Aoki, T. Namiki, S. Ohsaki, S. R. Saha, H. Sugawara, and H. Sato: J. Phys. Soc. Jpn. **71** (2002) 2098.
- 9) M. Kohgi, K. Iwasa, M. Nakajima, N. Metoki, S. Araki, N. Bernhoeft, J. M. Mignot, A. Gukasov, H. Sato, Y. Aoki, and H. Sugawara: J. Phys. Soc. Jpn. **72** (2003) 1002.
- 10) T. Tayama, T. Sakakibara, H. Sugawara, Y. Aoki, and H. Sato: J. Phys. Soc. Jpn. **72** (2003) 1516.
- 11) K. Kuwahara, K. Iwasa, M. Kohgi, K. Kaneko, N. Metoki, S. Raymond, M.-A. Méasson, J. Flouquet, H. Sugawara, Y. Aoki, and H. Sato: Phys. Rev. Lett. **95** (2005) 107003.
- 12) M. Yogi, H. Kotegawa, Y. Inamura, G.-q. Zheng, Y. Kitaoka, S. Osaki, H. Sugawara, and H. Sato: Phys. Rev. B **67** (2003) 180501.
- 13) K. Takegahara, H. Harima, and A. Yanase: J. Phys. Soc. Jpn. **70** (2001) 1190.
- 14) E. A. Goremychkin, R. Osborn, E. D. Bauer, M. B. Maple, N. A. Frederick, W. Yuhasz, F. M. Woodward, and J. Lynn: Phys. Rev. Lett. **93** (2004) 157003.
- 15) N. Takeda and M. Ishikawa: J. Phys. Soc. Jpn. **69** (2000) 868.
- 16) D. Adroja, J.-G. Park, E. Goremychkin, N. Takeda, M. Ishikawa, K. McEwen, R. Osborn, A. Hillier, and B. Rainford: Physica B **359–361** (2005) 983.
- 17) The excitation at 65 K in Ref. 16 is probably attributed to $\Gamma_1-\Gamma_4^{(1)}$ and not to $\Gamma_1-\Gamma_4^{(2)}$ since no maximum appears in $\chi(T)$.
- 18) I. Shirotni, T. Uchiumi, K. Ohno, C. Sekine, Y. Nakazawa, and K. Kanoda: Phys. Rev. B **56** (1997) 7866.
- 19) I. Shirotni: Rev. High Press. Sci. Technol. **6** (1997) 109.
- 20) D. J. Braun and W. Jeitschko: J. Solid State Chem. **32** (1980) 357.
- 21) I. Shirotni, J. Hayashi, T. Adachi, C. Sekine, T. Kawakami, T. Nakanishi, H. Takahashi, J. Tang, A. Matsushita, and T. Matsumoto: Physica B **322** (2002) 408.
- 22) M. Shimizu, H. Amanuma, K. Hachitani, H. Fukazawa, Y. Kohori, T. Namiki, C. Sekine, and I. Shirotni: submitted to J. Phys. Soc. Jpn.
- 23) E. Helfand and N. R. Werthamer: Phys. Rev. **147** (1966) 288.
- 24) N. R. Werthamer, E. Helfand, and P. C. Hohenberg: Phys. Rev. **147** (1966) 295.
- 25) T. D. Matsuda, K. Abe, F. Watanuki, H. Sugawara, Y. Aoki, H. Sato, Y. Inada, R. Settai, and Y. Ōnuki: Physica B **312–313** (2002) 832.
- 26) H. Sugawara, S. Osaki, S. R. Saha, Y. Aoki, H. Sato, Y. Inada, H. Shishido, R. Settai, Y. Ōnuki, H. Harima, and K. Oikawa: Phys. Rev. B **66** (2002) 220504(R).
- 27) E. D. Bauer, A. Ślebarski, E. J. Freeman, C. Sirvent, and M. B. Maple: J. Phys.: Condens. Matter **13** (2001) 4495.
- 28) M.-A. Méasson, D. Braithwaite, J. Flouquet, G. Seyfarth, J. P. Brison, E. Lhotel, C. Paulsen, H. Sugawara, and H. Sato: Phys. Rev. B **70** (2004) 064516.
- 29) S. V. Shulga, S.-L. Drechsler, G. Fuchs, K.-H. Müller, K. Winzer, M. Heinecke, and K. Krug: Phys. Rev. Lett. **80**

- (1998) 1730.
- 30) K. Maki and T. Tsuzuki: Phys. Rev. **139** (1965) A868.
- 31) A. A. Abrikosov: Sov. Phys. JETP **5** (1957) 1174.
- 32) Note that the inclusion of the secondary phase does not significantly affect the overall T -dependent behavior of κ_2 , although the resulting possible underestimation of ΔC may have led to the overestimation of κ_2 to some extent.
- 33) S. Ikeda, H. Shishido, M. Nakashima, R. Settai, D. Aoki, Y. Haga, H. Harima, Y. Aoki, T. Namiki, H. Sato, and Y. Ōnuki: J. Phys. Soc. Jpn. **70** (2001) 2248.
- 34) T. Kita: Phys. Rev. B **68** (2003) 184503.
- 35) G. Eilenberger: Phys. Rev. **153** (1967) 584.
- 36) K. R. Lea, M. J. M. Leask, and W. P. Wolf: J. Phys. Chem. Solids **23** (1962) 1381.
- 37) The fitting suggests that the other excited states lie probably above ~ 50 K in energy. Note that $\chi(T)$ is not reliable for the determination of high-energy CEF excitations.
- 38) P. Fulde, L. L. Hirst, and A. Luther: Z. Phys. **230** (1970) 155.
- 39) P. Fulde and J. Jensen: Phys. Rev. B **27** (1983) 4085.